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SYNTHESIS OF POLYMER-SUPPORTED REAGENTS AND THEIR CATALYTIC PROPERTIESAND APPLICATIONS

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ABSTRACT

This paper presents a review summary of hypervalent Iodine compounds reflects a wide variety beneficial in chemical transformation. The use of hypervalent iodine reagents as catalysts in synthetic transformations. It was planned to use polymer-supported hypervalent iodine reagents as catalysts. These reagents are prepared by per acid oxidation of iodopolystyrene. During reaction, stoichiometric amount of polymeric iodine (III) reagent is required and after completion of reaction, polymeric iodine (III) reagent is reduced to monovalent iodine (I) as side product, which was initially employed for the production of iodine (III) species as outlined.

***Keywords**:- Polymers; agrochemical research; Stoichiometry; polystyrene; Polymer supported; Polymerization; Hypervalent compounds; Iodine reagents*

INTRODUCTION

The polymer supported reagents were prepared by Chemical modifications of preformed polymers and Polymerization of functional monomers. Hypervalent iodine reagents have found broad applications in organic chemistry and are now-a-days frequently employed in various synthetic transformations. Because these are non metallic oxidation reagents, they avoid the issue of toxicity of many transition metals commonly involved in such processes. Synthetic use of hypervalent iodine compounds like iodobenzenediacetate (IBD,), bis (trifluoroacetoxy) iodobenzene (BTI), [hydroxy (tosyloxy)] iodobenzene (HTIB, 28), ([hydroxy (mesyloxy)] iodobenzene (HMIB, 29), dichloroiodobenzene (DCIB, 30), difluoroiodobenzene (DFIB, 31) has been extensively studied (Figure 1.1.4). These reagents carry out the reactions at mild reaction conditions and are easy to handle, resulting in high chemo selectivity and low toxicity.

$$\underset{\text{S-reagent/catalyst}}{P-X} \quad + \quad \text{Substrate} \longrightarrow \text{Product} \quad + \quad \underset{\text{spent polymer by product}}{P-Y}$$

Reaction on a polymer support

$$\text{R OH} \xrightarrow[H_2O,))),\ r.t.]{\text{PS-IBD, KBr}} \text{Ketones or Carboxylic acids}$$

The polymeric reagents are easier and safer to handle than their low molecular weight analogs. Toxic, noxious or hazardous reagents and their byproducts can be immobilized and therefore not released into solution thereby improving their general acceptability, utility and safety profile.

MATERIALS AND METHODS

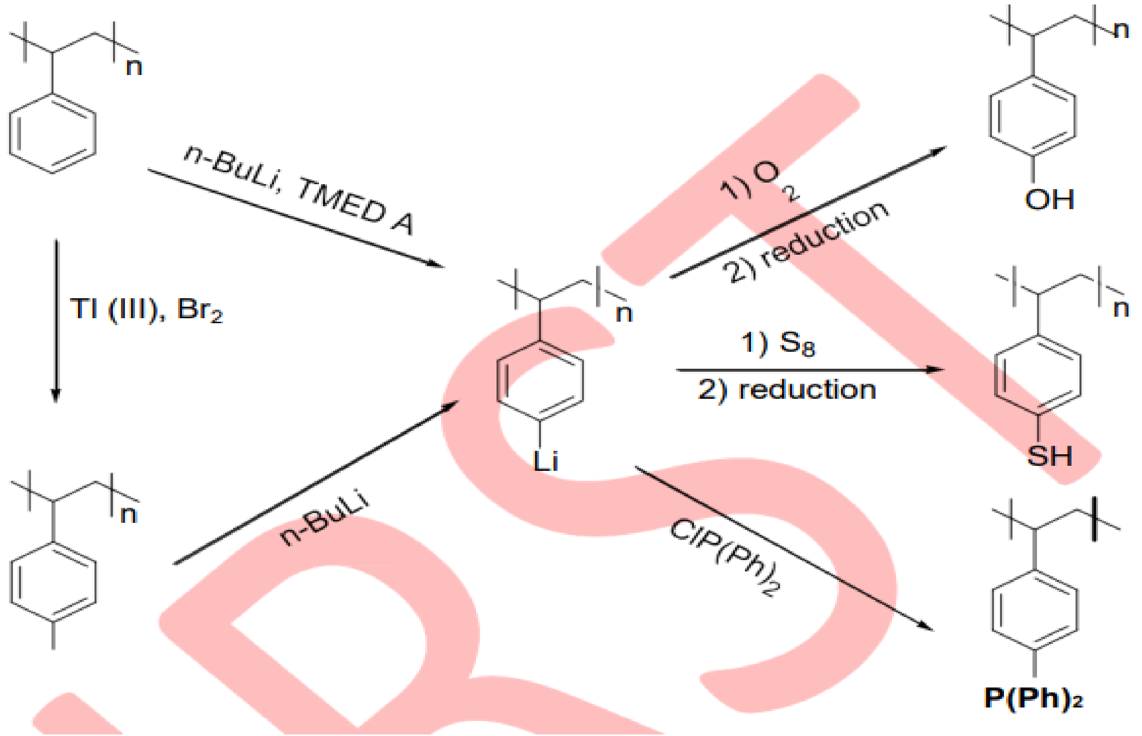
Most of the work has been carried out on cross-linked polystyrene. The modification of cross-linked polystyrene, besides chloromethylated polystyrene, includes ringbrominated or ring-lithiated polystyrene. The ring lithiated polystyrene resins are of particular interest due to the wide variety of otherwise in accessible functionalities, which can be ultimately introduced. The number of reactive ends in the polymer chain can be reduced by addition of a co-monomer and insoluble resins are obtained in the presence of a cross-linked difunctional co-monomer.

METHODOLOGY

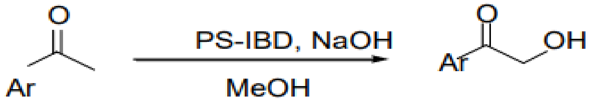
There are many procedures for the preparation of polymer-supported reagents like Chemical modifications of preformed polymers, Polymerization of functional monomers, Polymer-Supported Hypervalent Iodine Reagents etc.

Reactions

The number of reactive ends in the polymer chain can be reduced by addition of a co- monomer and insoluble resins are obtained in the presence of a cross-linked difunctional co-monomer. This approach has been used successfully in the preparation of polymer- supported reagent containing pyridine residues and benzaldehydes or phosphine units. Ring-lithiated polystyrene can be transformed into polymer-bound phenol or thiophenol or diphenylphosphine.



PS-IBD is one of the most common polymer-supported hypervalent iodine reagentsserving as an excellent substitute for its low molecular analog IBD.



Ar = C_6H_5, 4-$CH_3C_6H_4$, 2, 4, 6-$(CH_3)_3C_6H_2$

PS-IBD has been efficiently utilized in producing a variety of heterocycles.

Procedure

Reactions involving polymeric reagents can be optimized and scaled up extremely readily because they can be constantly monitored using conventional methods (TLC, LC- MS, GC-MS, NMR, etc.). Additionally, because the chemistry is carried out in solution, it often requires minimal optimization compared to that involved in transferring a solution-phase reaction onto a polymer-bound substrate. The reaction involving functionalized polymer is designed in such a way as to allow the spent polymer by- product to be recovered quantitatively and regenerated without appreciable loss of activity, like Ease of handling; Analogs of hygroscopic, pyrophoric and explosive reagents; Analogs of odorous reagents; Analogs of toxic reagents; Stoichiometry of the reagent; Simultaneous use of more than one reagent; Microenvironment effects; Site-site interactions; Polymer-supported reactants are usually prepared in the form of beads of about 50–100 micrometers' diameter. In a typical application of reactions involving polymer-supported substrates, a substrate is first attached to an appropriately functionalized polymer support. The synthetic reactions of interest are then carried out onthe supported species. Finally, the product is detached from the polymer and recovered.

Reactions involving polymer-supported reagents are generally more useful than those involving polymer-supported substrates, because no attachment or detachment reactions are needed, and it is not necessary for all the polymer-supported species to react in high yield. Indeed, polymer supported reagents are often used in excess to drive reactions to high conversions. Polymer supported catalysts are the most attractive type of polymer- supported reactants.

RESULTS

In the present study, 2% cross-linked polystyrene was firstly iodinated with molecular iodine, iodine pentaoxide and sulfuric acid on refluxing in a mixture of nitrobenzene and carbon tetrachloride for 24h to produce iodopolystyrene (PS-I). PS-I was quantitatively acetoxylated with per acetic acid generated *in situ* from a stirred solution of acetic anhydride and 30% hydrogen peroxide to afford polymer-supported iodobenzene diacetate (PS- IBD,) in excellent yield.

DISCUSSION

The synthesized polymer-supported hypervalent iodine reagents were characterized using physical methods as well as IR and thermal studies [differential scanning calorimetry (DSC) and thermogravimetry (TG)]. All the polymer- supported hypervalent iodine reagents (PS-IBD, PS-BTI, PS-HTIB and PS- HMIB) showed the presence of C-H stretching and aromatic ring stretching bands (vide experimental). The carbonyl stretching bands in PS-IBD and PS-BTI were observed respectively at 1650 and 1659 cm-1. Thermal behavior of hypervalent iodine reagents and polymer- supported hypervalent iodine reagents (PS-IBD, PS-BTI, PS-HTIB and PS-HMIB) including that of polystyrene and iodopolystyrene was investigated by TG and DSC. TG is the branch of thermal analysis which examines the mass of a sample as a function of temperature. It is used to characterize the decomposition and thermal stability of materials.

SUMMARY

The use of hypervalent iodine reagents as catalysts in synthetic transformations has attracted recent attention. Encouraged by the ability of iodoarenes, when present in catalytic amounts, resulting in an equally efficient synthetic transformation as present in stoichiometric amounts, it was planned to use polymer-supported hypervalent iodine reagents as catalysts. These reagents are prepared by per acid oxidation of iodopolystyrene. During reaction, stoichiometric amount of polymeric iodine (III) reagent is required and after completion of reaction, polymeric iodine (III) reagent is reduced to monovalent iodine (I) as side product, which was initially employed for the production of iodine (III) species as outlined.

In brief, polymer-supported hypervalent iodine reagents can also be used in catalytic amounts in various chemical transformations and results in equally effective transformation. Stoichiometric amount of iodine (III) is thereby not required making the synthetic transformation economical as well as ecofriendly.

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